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THE PREPARATION OF BERYLLIUM FROM GADOLINITE RESIDUES

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Mr Alfred Werner Meyer

ENTITLED The Preparation of Beryllium from Gadolinite Residues.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

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Table of Contents

Introduction	1
The Composition and Occurrence of Gadolinite	2
The Gadolinite Residues	4
The Preparation of Beryllium Basic Carbonate from the Gadolinite Residues	5
The Preparation of Sodium Beryllium Fluoride	8
Sketch of Apparatus used in the Electrolysis	11
The Electrolysis of the Fused Sodium Beryllium Fluoride	12
The Purification of the Metallic Beryllium	16
The Recovery of the Beryllium Salts	18
Summary	19

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THE PREPARATION OF BERYLLIUM FROM GADOLINITE RESIDUES

Introduction

The purpose of this investigation was to devise a method for the preparation of pure metallic beryllium from gadolinite residues that had accumulated in the chemical laboratory of the University of Illinois from previous work on yttrium earths. The residues were very rich in beryllium and it was very desirable that a method be found by which they could be converted into a saleable product or a product upon which further research work could be done. It was also found desirable to devise a process which was applicable to the preparation of beryllium from gadolinite.

The investigation includes the preparation of a pure beryllium salt from the residues, the preparation of metallic beryllium from the pure salt, the purification of the metallic beryllium, and the recovery of the beryllium salts that were not converted into the metal.

The Composition and Occurence of Gadolinite[1]

Gadolinite, $Be_2Fe(YO)_2(SiO_4)_2$ or 2 BeO. FeO·$2Y_2O_3$.$2SiO_2$, occurs in granitic pegmatite in Llano Co., Texas and is associated with allanite, yttrialite, uranite, gummite, crytalite, molybdenite, and other minerals. It also occurs in granite pegmatite with allanite, topaz, cassiterite, and fluorite, at Devil's Head Mountain, Douglas Co., Colo. In granite veins, on Hittero" Fleckefjord, Norway; near Falun, and at Ytterby, Sweden; in Silesia; New Castel, Mourne mountains, Ireland, and in granite of Cooglegong tin fields, Western Australia.

An analysis of Llano Co., Texas, gadolinite gave the following composition.-

SiO_2	23.79
ThO_2	.58
Y_2O_3) Er_2O_3)	41.65
Ce_2O_3	2.62
Di_2O_3) La_2O_3)	5.22
Al_2O_3	----
Fe_2O_3	.96
FeO	12.42
MnO	----
BeO	11.33
CaO	.74
Na_2O	-----

[1]Rock Minerals By Iddings.

P_2O_5	.05
H_2O	1.03

The Gadolinite Residues.

The gadolinite was crushed, powdered, and a mixture of concentrated sulfuric and hydrochloric acids added. Heat was applied until white fumes were evolved and the sulfated mineral was then stirred with water in a large tank, care being taken not to do this too rapidly because of the heat evolved. After settling, the clear liquid was decanted and the rare earths precipitated with oxalic acid. The filtrate, which contained the beryllium and iron, was oxidized to remove the excess oxalic acid, and evaporated down until it was about one-half liquid and one-half solid. In this form it made up the gadolinite residues. The residue was very strongly acid and an attempt was made to drive off the acid by evaporation. However this proved impracticable. A small average sample was evaporated to dryness and a determination for beryllium made on the dry sample according to the method of C. L. Parsons[2] giving a result of 31.2 per cent BeO.

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[2]The Chemistry and Literature of Beryllium.

The Preparation of Beryllium Basic Carbonate from the Gadolinite Residues.

About 3000 grams of the residue were dissolved in water, in which it was completely soluble, and a small amount of nitric acid added in order to oxidize any ferrous iron which might be present. One liter of ammonium hydroxide was added, followed by concentrated sodium hydroxide solution until the odor of NH_3 made its appearance. The filtrate gave no test for beryllium upon further addition of sodium hydroxide. Considerable difficulity was encountered in filtering off the precipitate which was composed of beryllium and ferric hydroxides. It was finally found necessary to resort to the use of a filter press using double thickness canvas as the filtering medium. Water, made slightly alkaline with NH_4OH, was forced through the filter press in order to wash the precipitate free from occluded liquid. The filtrate and washings were discarded. The precipitated hydroxides were removed from the filter press and stirred with enough hydrochloric acid to dissolve about two-thirds of the whole mass. This brought all of the beryllium into solution and left a large per cent of iron behind. The residue was tested and proved to contain but a slight trace of beryllium, so it was discarded. The acid extract was filtered, heated to boiling, and carefully precipitated with a concentrated sodium hydroxide solution until a small amount of the filtered liquid gave a light colored precipitate with ammoniumhydroxide, showing that nearly all of the iron had been removed. The liquid and precipitate were

separated by means of the filter press.

An attempt was made to remove the rest of the iron by the method recommended by C. James and G. A. Perley[3], namely, by adding sodium hypobromite and sodium hydrogen sulfide but this proved impractical in this case as the final product was contaminated by pollysulfides and other impurities, Therefore, the method based on the total insolubility of ferric hydroxide in a ten per cent boiling sodium bi-carbonate solution and on the total solubility of beryllium hydroxide in the same was used.[4]

The liquid, from which most of the iron had been removed, was evaporated on a steam bath until crystals of salt started separating out, divided into five equal parts to facilitate handling, and each part added, with stirring, to six liters of boiling saturated solution of sodium bi-carbonate and the whole heated to boiling. After cooling, the clear liquid was decanted and the remainder filtered off. The precipitate was washed with a ten per cent solution of sodium bi-carbonate until the washings showed no test for beryllium. The washings were added to the filtrate. The filtrate was now carefully acidified with hydrochloric acid, heated to boiling, and the beryllium precipitated out as the basic carbonate by adding a saturated sodium carbonate solution. After thorough boiling, the precipitated basic carbonate was filtered off, well washed with boiling water,

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[3] J. A. C. S., 38, 875 (1915)

[4] J. A. C. S., 28, 1589 (1906)

and dried at 100°C.

The beryllium basic carbonate thus obtained was pure white and entirely soluble in sodium bi-carbonate which according to Parsons is a very delicate test for purity. The only impurity present was sodium carbonate which had been occluded by the precipitate. It was not necessary to remove this because the basic carbonate was used in making sodium beryllium fluoride. A sample of the basic carbonate was ignited and proved to contain 26.1 per cent BeO.

The Preparation of Sodium Beryllium Fluoride

Although Warren[5] claimed to have prepared metallic beryllium by the electrolysis of the bromide and Borchers[6] proposed the preparation by means of electrolyzing the chloride, mixed with a alkali chloride, these methods have proven unsuccessful. Lebau[7] shows that the halides of beryllium do not conduct electricity but that the fluoride of beryllium mixed with either sodium fluoride or potassium fluoride prove an excellent conductor and can be easily electrolyzed. Marignac[8] shows that beryllium forms two double fluorides with sodium, namely, $NaBeF_3$ and Na_2BeF_4. It has also been shown that fused beryllium fluoride is soluble in all proportions in fused sodium fluoride. Therefore there is a great number of possible combinations in making up the salt to be electrolyzed. It is desirable to have a fusion containing a large per cent of beryllium fluoride because the melting point of beryllium fluoride is only 800°C while that of sodium fluoride is 980°C. An increase in the amount of beryllium fluoride in the salt will therefore lower the temperature at which it is necessary to work. It is desirable to keep the temperature as low as possible in order to minimize the oxidation of the metallic beryllium formed. Beryllium fluoride is very soluble in water while sodium fluoride is only slightly so. This is another

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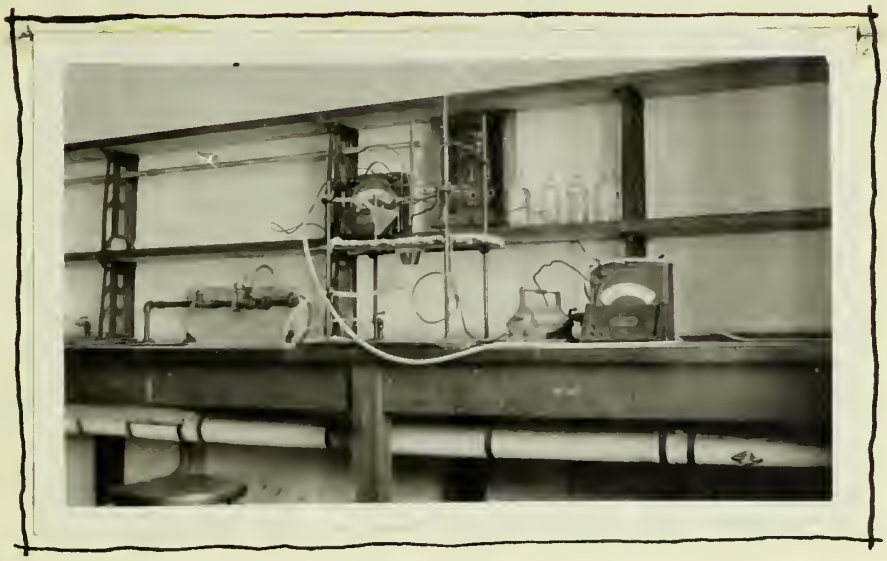
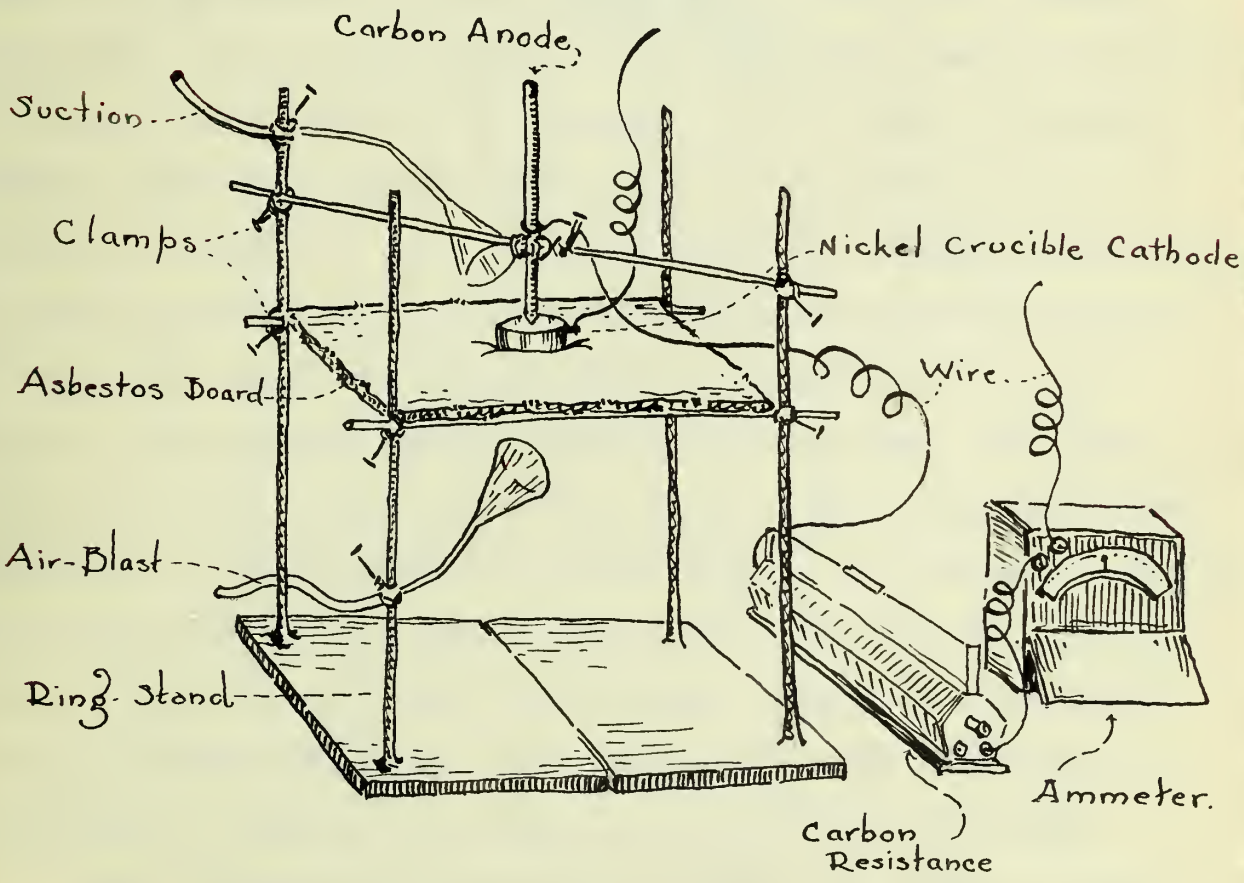
[5]Ztsch. f. Anorg. Chem., 13, 364.
[6]Ztrch. f. Elektrochem. 2 3, 9.
[7]Ann. Chim. et Phys. (7) 16, 460.
[8]Ann. Chim. et Phys. (4) 30, 45

point in favor of a high beryllium fluoride content because the purification of the metal depends largely upon the solubility of the fluorides in water. However, as has been shown before, the fluoride of beryllium does not conduct electricity. Therefore the salt to be electrolyzed should not contain too much beryllium fluoride or the conductivity of the melt will be very low and it will be necessary to use a high voltage in electrolyzing the salt. If the resistance of the molten salt is very high there will be great danger of overheating. This tends to cause the metallic beryllium formed to oxidize or to alloy with the nickel crucible. Taking all of these things into consideration it was decided to use the salt of the formula $NaBeF_3$. It was made as follows.-

125 grams of 48 per cent hydrofluoric acid were weighed out into a platinum evaporating dish and to this were added 53 grams of pure analyzed sodium carbonate, care being taken to add it in small amounts in order to prevent losses by frothing or spattering. 50 cc. of distilled water were added and enough beryllium basic carbonate to neutralize the solution. It was found that it required 100 grams of the beryllium basic carbonate. This agrees approximately with the theoretical amount calculated from the results of the analysis of the basic carbonate. The solution was then evaporated to dryness over a low flame, care being taken to prevent losses by spattering. It was then fused and allowed to cool. After cooling, the salt was removed from the dish and broken up into small pieces. The yield was 90 grams of sodium beryllium fluoride. The double fluoride thus prepared was transparent, easily fusible, and

completely soluble in water.




Carbon Anode
Suction
Clamps
Nickel Crucible Cathode
Asbestos Board
Wire
Air-Blast
Ring Stand
Ammeter.
Carbon Resistance

D.V.C. del.

The Electrolysis of the Fused Sodium Beryllium Fluoride.

The apparatus for the electrolysis of the fused sodium beryllium fluoride consisted of two double iron ring stands clamped together by two horizontal iron rods about eight inches from the base. These rods served to support a heavy sheet of asbestos board which in turn, served to support a nickel crucible. It also acted as an insulator, and protected the fused salt from contamination by the conbustion gases from the burner used in preheating. The nickel crucible which served as the cathode, was of about 200 cc. capacity and was tightly fitted into a round opening in the asbestos board. A horizontal iron rod, clamped diagonally to two of the vertical ring stand rods, served to support the carbon anode which was so arranged that it could be raised or lowered. The carbon anodes used varied in size from .5 cm. to 2.5 cm. in diameter. The 1 cm. rods proved to be more satisfactory. The gases produced by the electrolysis were carried off through a glass funnel bent so that the mouth of it projected over the crucible. The funnel was attached to a vacuum pump. The preheating was done by means of a four-flame burner placed under the crucible. It was necessary to devise a means of cooling the crucible during the electrolysis because the current produced an intense heat. At high temperatures nickel alloys easily with beryllium giving a low melting alloy. The cooling was done by forcing compressed air against the bottom and sides of the crucible.

Four different runs were made varying the length of time of each run in order to determine what conditions would give the

best yeild of beryllium.

The first run was made using 90 grams. of $NaBeF_3$ and 10 grams of BeO. The salt was first broken up into small pieces, placed in the crucible and melted. A carbon rod 1 cm. in diamter, acting as the anode, was lowered into the fused ma ss until it was about 1 cm. from the bottom of the crucible. The circuit was then closed. An attempt was made to use a 12-volt generator as the source of current and in another instance storage batteries giving 28 volts. However, both of these proved unsatisfactory because they did not give a high enough current, and it was found necessary to use a 110-volt generator. The current was regulated by means of a carbon resistance and kept constant at 6 amperes throughout the four runs. The difference in potential between the two electrodes remained constant at 87 volts during the first run. After one and three quarters hours, the electrolysis was discontinued and the fused mass allowed to cool. It was then removed from the crucible, ground up, and treated to remove the metallic beryllium. The yield was found to be 0.57 grams of 98 per cent berryllium.

In the second run, 90 grams of $NaBeF_3$ were electrolyzed for three hours using a constant current density of 6 amperes. The difference in potential across the electrodes was 84 volts. At the end of three hours the voltage across the electrodes rose to 110 and the current dropped down to 0. The crucible was removed while still hot and the lower part of it plunged into cold water. This caused the electrolyte to fall apart into a fine gray powder and saved the trouble of grinding it. The yield from this run was found to be 1.20 grams of 98 per cent beryllium.

In the first two runs, considerable difficulty was caused by the anode effect. In the third run this was eliminated to a large extent by using a carbon anode 2.5 cm. in diameter. However, it was found that the large carbon anode favored the formation of beryllium carbide. The electrolysis was carried on much the same as in the first two runs, using a charge of 90 grams of $NaBeF_3$. The current was kept constant at 6 amperes and the difference in potential across the electrodes was found to be 54 volts. After three hours the current dropped down to 0 and the mass solidified. The burner was then placed under the crucible and the electrolysis carried on for another hour when it was noticed that the crucible was beginning to fall apart. The electrolysis was then discontinued and the mass allowed to cool. It was found that a part of the beryllium had alloyed with the crucible and formed a low melting beryllium-nickel alloy. The beryllium which had not alloyed with the crucible had been oxidized or changed to the carbide by contact with the large carbon anode and but a slight trace of beryllium was found in the mass.

The loss of the beryllium in the third run was attributed to using too large a carbon anode, thus favoring the formation of beryllium carbide, and to heating up the walls of the crucible with the burner, thus causing the oxidation of the beryllium and the formation of the beryllium-nickel alloy. In the fourth run an attempt was made to eliminate these unfavorable conditions and still make a long run. Seventy five grams of $NaBeF_3$ were electrolyzed using a carbon anode 0.5 cm. in diameter. The difference in potential across the electrodes was found to be 95 volts. The

current was kept constant at 6 amperes by adding in small amounts, from time to time, 65 grams more of $NaBeF_3$. In this way the run was continued for five hours without finding it necessary to use external heat. However, at the end of five hours the crucible began to give way and the run was discontinued. It was found that the beryllium had either alloyed with the crucible or formed the oxide or carbide and that but very little of the metal was present.

The results of the four runs show that the best yield of beryllium can be obtained by electrolyzing small amounts of the $NaBeF_3$ for a short time, taking great care to keep the walls of the crucible cool. Long time runs cause the oxidation of the metallic beryllium, the formation of beryllium carbide, the volitalization of the beryllium fluoride, and the alloying of the metallic beryllium with the nickel crucible.

The Purification of the Metallic Beryllium

The fused salt was examined after the electrolysis and proved to contain metallic beryllium, sodium fluoride, beryllium fluoride, beryllium carbide, and beryllium oxide. Sodium fluoride and beryllium fluoride are soluble in water, beryllium carbide is decomposed by it, and metallic beryllium is but slightly effected. Therefore, beryllium and beryllium oxide can be easily separated from the other salts by treatment with water. However, metallic beryllium is soluble in acid or alklaine solutions. Therefore great care must be taken in order to keep the solution neutral. The fusion mixture was ground to a fine powder in a mortar and added, a small amount at a time, to large portions of distilled water. The solution was kept neutral by running in a very dilute solution of hydrochloric acid. This was done to prevent the beryllium from being attacked by the alkaline solution and to prevent the formation of beryllium hydroxide by the decomposition of the beryllium carbide. The solution was then decanted, saved, and later treated to recover the beryllium salts. The beryllium was then treated with successive portions of boiling water until the washings gave no test for beryllium salts. The beryllium, together with the beryllium oxide was then washed onto a filter paper and dried. The next step was to separate the beryllium and the beryllium oxide. An attempt was made to separate the beryllium and beryllium oxide by shaking with mercury. This proved unsuccessful because the beryllium would not amalgamate with the mercury.

The specific gravity of beryllium oxide is known to be

3.01 while the specific gravity of metallic beryllium is 1.85. It is therefore very easy to separate the two mechanically. The impure beryllium was centrifuged in a mixture of ethylene bromide and alcohol having a specific gravity of 1.90. The beryllium oxide was thrown to the bottom of the liquid while the pure beryllium remained on top. This operation was repeated several times until all of the beryllium oxide had been removed. The pure beryllium was then washed with several portions of alcohol, then with ether, and finally dried at 100°C.

The beryllium thus obtained was analyzed by the gas-volumetric method which consists of measuring the amount of H_2 given off by the reaction $Be + 2HCl = BeCl_2 + H_2$, and was found to be 98 per cent pure.

The Recovery of the Beryllium Salts.

Inasmuch as pure beryllium salts are of considerable value, it was very desirable to recover them. The washings containing the beryllium salts were acidified with hydrochloric acid and ammonium hydroxide added to precipitate the beryllium as beryllium hydroxide. The precipitate was allowed to settle and the clear liquid decanted. The beryllium hydroxide was filtered off, washed with water containing a small amount of sodium hydroxide, then with distilled water, and finally dried at 100°C.

The beryllium hydroxide thus recovered contains a trace of sodium hydroxide. However, this need not be removed as it is to be used in making $NaBeF_3$.

Summary

The results of this investigation show that pure metallic beryllium can be easily prepared from gadolinite residues. It can also be obtained from gadolinite by first treating the gadolinite in such a manner as to obtain the residues.

Pure beryllium basic carbonate is obtained from the gadolinite residues by the removal of most of the iron through fractional precipitation as the hydroxide, and by dissolving the beryllium hydroxide formed, in a saturated sodium bi-carbonate solution. The beryllium is precipitated as the basic carbonate by acidifying and adding a strong solution of sodium carbonate.

The halides of beryllium do not conduct electricity, but mixed with alkali halides, they prove excellent conductors. A salt of the composition $NaBeF_3$ was prepared by dissolving the calculated amounts of sodium carbonate and beryllium basic carbonate in hydrofluoric acid, evaporating to dryness, and fusing.

The metallic beryllium was prepared by electrolyzing the fused $NaBeF_3$. Four runs were made and the results show that the best yield of beryllium is obtained by electrolyzing small amounts of the $NaBeF_3$ for a short time. Care should be taken to keep the walls of the crucible cool in order to prevent the oxidation of the metallic beryllium, and the formation of a nickel-beryllium alloy.

The metallic beryllium was purified by dissolving the soluble impurities in water, and was separated from beryllium oxide

by centrifuging in a mixture of ethylene bromide and alcohol having a specific gravity of 1.90. The combined runs yielded 1.77 grams of 98 per cent metallic beryllium.

The beryllium salts, dissolved in the washings from the purification process, were recovered as hydroxides.

In conclusion, the author wishes to take this opportunity of thanking Dr. B. S. Hopkins for his many helpful suggestions and the interest shown in the solution of this problem.

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